# CAUSES OF FOAMING OF IRON-CONTAINING MELTS

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The reasons for the increased tendency to foam formation in iron-containing glass melts depending on their composition, iron oxide concentration, and the melting medium are identified. The recommendations for the elimination of these reasons are provided. It is demonstrated that the foam in the iron-containing silicate melts is formed in the course of interaction of the ferritized melt and quartz.

One of the problems in the synthesis of iron-containing glasses consists in glass foaming in the stage of melting. It was discussed by numerous researchers who studied these glasses in the context of using them to produce glass ceramics. However, no comprehensive study of this phenomenon, its dependence on various factors, and methods for its possible prevention was carried out [1, 2]. And yet such comprehensive research is essential for the development of industrial technology for production of glass ceramics based on industrial wastes, slag and ashes from thermal power plants which contain iron oxides, since the foaming process extends the melting zone inside the glass-melting furnace and prevents thorough heating of the glass melt inner layers, which has a significant effect on glass quality.

There are three known reasons for the emergence of excessive foam in the glass-melting stage [3]: excessive gas emission after the batch surface layer is melted; excessively high heating rate of the melting batch; and the effect of surfactants which increase the strength of the melt film.

The surface activity of the melt primarily depends on its composition, especially on the presence of small quantities of additives. In particular, $Fe_2O_3$ and $Cr_2O_3$ are known to be surface-active, whereas FeO does not belong to this category.

The present study mostly considers the effect of the chemical composition of glass on the process of iron-containing melt foaming.

Foaming was investigated on iron-containing glasses: hedenbergite, augite-hedenbergite, as well as diopside-hedenbergite with different contents of chromium oxide (1HD – 3HD) and wollastonite glasses with different contents of fluorine (1W – 3W) synthesized from ashes from the Krasnoyarsk condensation power plant (Table 1).

The mixtures were placed in a corundum crucible of 10 ml capacity, heated in a Silit furnace up to the considered temperature and held for 15 min within the temperature range of 1000 – 1500°C. Next, the crucible was cooled in air. The nature of the foam was evaluated visually, as well as by measuring the melt froth thickness and the average diameter of emerging bubbles. The variation in the valence of iron and chromium in the melt resulting from heating mixtures of the

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**TABLE 1**

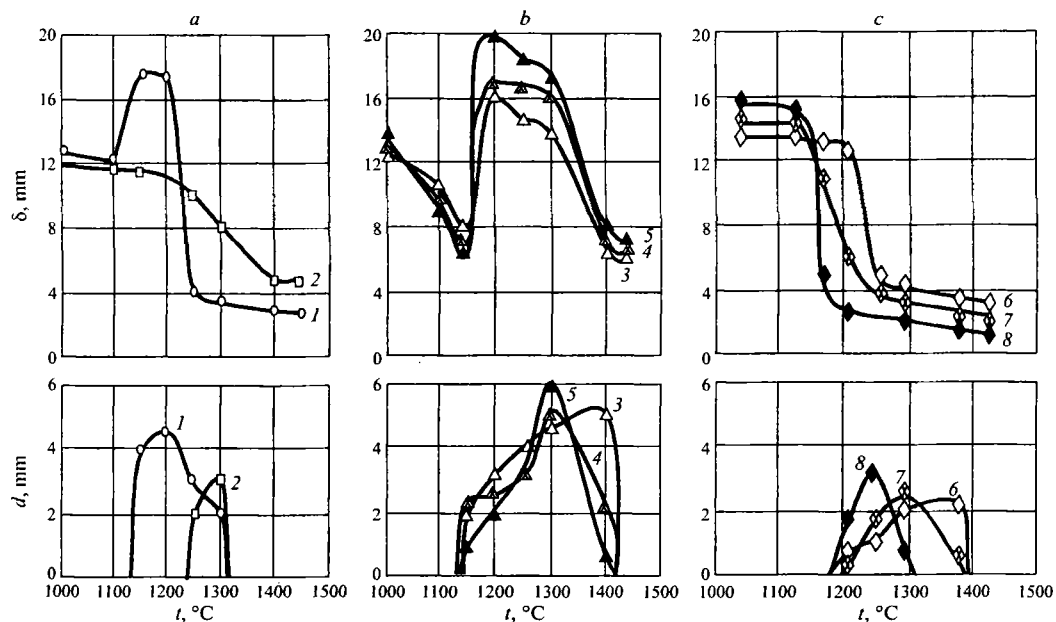| Glass | Mass content, % | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | CaO | MgO | $K_2O$ | FeO | $Cr_2O_3$ | $F^-$ |
| Hedenbergite | 48.39 | – | 22.58 | – | – | 29.03 | – | – |
| Augite-hedenbergite | 38.67 | 21.87 | 15.41 | – | – | 24.05 | – | – |
| Diopside-hedenbergite: | | | | | | | | |
| 1HD | 60.00 | 8.00 | 28.00 | 4.00 | – | 10.00* | – | – |
| 2HD | 60.00 | 8.00 | 28.00 | 4.00 | – | 10.00* | 0.50* | – |
| 3HD | 60.00 | 8.00 | 28.00 | 4.00 | – | 10.00* | 1.50* | – |
| Wollastonite: | | | | | | | | |
| 1W | 63.63 | 6.36 | 20.91 | 2.73 | 6.37 | 5.00* | – | – |
| 2W | 63.63 | 6.36 | 20.91 | 2.73 | 6.37 | 5.00* | – | 2.50* |
| 3W | 63.63 | 6.36 | 20.91 | 2.73 | 6.37 | 5.00* | – | 3.00* |

\* Above 100‰.

**Fig. 1.** Variation in thickness δ of the frothed glass melt layer and the bubble average size $d$ with increasing temperature $t$: $a$) hedenbergite ($1$) and augite-hedenbergite ($2$) mixtures; $b$) diopside-hedenbergite mixtures without chromium oxide ($3$); with 0.5 $Cr_2O_3$ ($4$) and with 1.5% $Cr_2O_3$ ($5$); $c$) iron-containing wollastonite mixture based on ashes from Krasnoyarsk power plant without fluorine ($6$), with 2.5% F ($7$), and with 3% F⁻ ($8$).

diopside-hedenbergite compositions was studied using the reflection spectra at a wavelength of 340 – 820 nm. The phase transformations in the mixtures occurring under heating were investigated using the x-ray phase analysis method.

In additions to this, the foaming capacity of the glasses was ranked over a five-grade scale, taking into account the foaming interval and the height of the frothed melt layer (Table 2). The maximum valuation (grade 5) corresponded to the minimum temperature interval of foaming and the lowest height of the frothed glass melt. The glasses were also evaluated with respect to their potential for being melted in tank furnaces.

Estimating the temperature interval of fluid glass foaming is important in designing tank furnaces, since as the temperature interval increases, the size of the frothed layer and the extent of the froth surface increase as well. Consequently,

to order to accomplish complete clarification of certain iron-containing glasses, the furnace melting tank may have to be extended.

As can be seen in Fig. 1, foaming during iron-containing glass melting is most completely characterized by the thickness of the frothed glass melt layer. Whereas augite-hedenbergite and iron-containing wollastonite mixtures exhibit a gradual decrease in the thickness of the emerging glass melt, as the batch melts, hedenbergite and diopside-hedenbergite mixtures exhibit an abrupt increase in thickness.

Glass melting indicated that intense foaming in the hedenbergite mixture occurs within the temperature range of 1150 – 1200°C. The bubble size in the foam layer is 2 – 5 mm. The maximum increase in the thickness of the frothed glass melt layer occurs at a temperature of 1200°C, and the

**TABLE 2**

| Glass | Temperature interval of intense foaming, °C | Δt, °C | Foaming intensity and interval ranking | Potential for use in production of glass ceramics |
|---|---|---|---|---|
| Hedenbergite | 1150 – 1300 | 150 | 2 | No |
| Augite-hedenbergite | 1250 – 1300 | 50 | 5 | Yes |
| Diopside-hedenbergite: | | | | |
| 1HD | 1150 – 1400 | 250 | 1 | No |
| 2HD | 1150 – 1400 | 250 | 1 | The same |
| 3HD | 1150 – 1300 | 150 | 2 | The same |
| Wollastonite: | | | | |
| 1W | 1250 – 1400 | 200 | 2 | The same |
| 2W | 1200 – 1300 | 100 | 4 | Yes |
| 3W | 1200 – 1300 | 100 | 4 | The same |
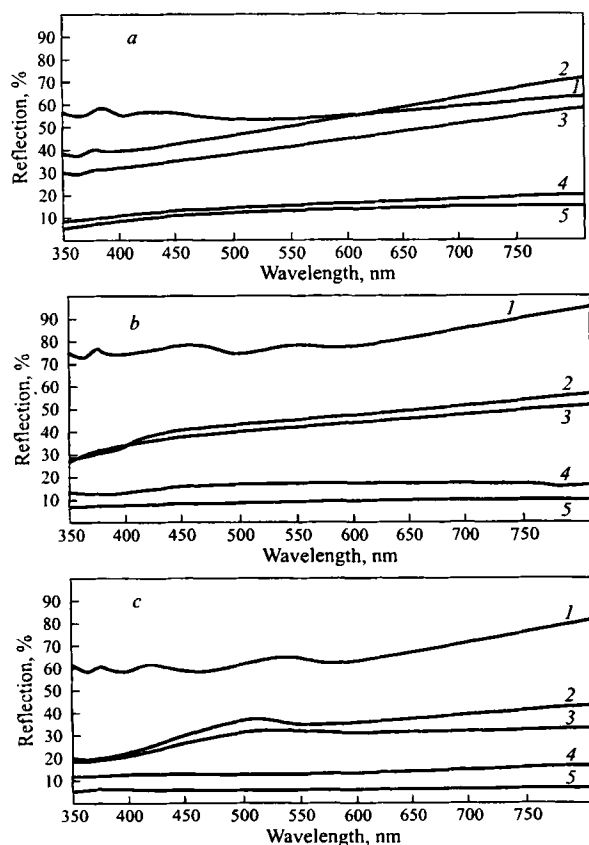
**Fig. 2.** Reflection spectra of diopside-hedenbergite mixtures heat-treated for 15 min: *a, b, c*) 1HD, 2HD, and 3HD, respectively; *1* ) initial mixture; *2, 3, 4, 5* ) mixtures heat-treated at temperatures of 1050, 1100, 1200, and 1450°C, respectively.

average bubble diameter attains 5 mm. The temperature interval of intense foaming is 150°C.

When an augite-hedenbergite mixture is used, substitution of aluminum oxide for a part of the iron oxide causes the mixture to melt in the higher temperature range of 1250 – 1300°C. According to the x-ray phase analysis, at these temperatures, refractory aluminum-containing crystalline phases of anorthite $CaAl_2SiO_8$ and helenite $Ca_2Al_2SiO_7$ are formed, which dissolve in the melt and thus increase its viscosity and delay the process of bubble formation. The intensity of bubble formation in the augite-hedenbergite mixture is not as high as in the hedenbergite mixture. No increase in the frothed melt thickness occurs in this case. It can be stated that the substitution of aluminum oxide for a part of iron oxide decreases the tendency of the melt to foam formation.

At the same time, in spite of the increased viscosity of the melt, the higher melting temperatures of the augite-hedenbergite mixtures lead to the separation of the emergent bubbles, especially since the average bubble diameter is sufficiently large (2 – 4 mm). As a consequence, the foaming temperature range of these glasses is only 50°C.

The foam-formation process in the diopside-hedenbergite mixtures starts at a temperature of 1150°C and ends at 1400°C. As can be seen in Fig. 1*b*, a chromium oxide additive increases the foaming intensity and the bubble size. In this case, according to the data in [4], the following equilibrium between the chromium oxides and the iron oxides is established in the glass melt:

$$4CrO_3 = 2Cr_2O_3 + 3O_2\uparrow.$$
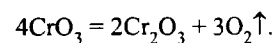
With the simultaneous presence of the chromium oxides and iron oxides in the melt, the following reaction is possible [5]:

$$12FeO + 8CrO_3 = 6Fe_2O_3 + 4Cr_2O_3 + 3O_2\uparrow.$$
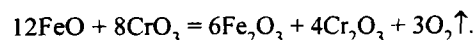
As can be seen from the above equations, a shift of the equilibrium as the result of the redox reactions will facilitate additional release of oxygen, which can increase the foaming intensity. Moreover, chromium oxide, which is a surfactant, significantly decreases the surface tension of the melt [5], which will also contribute to the formation of stable foam on its surface.

In melting chromium-containing diopside-hedenbergite mixtures, the degassing of the fluid glass occurs within a more narrow temperature interval ($\Delta t = 150°C$), as compared to the chromium-free mixture with 10% FeO, i.e., it can be said that additional release of gas (oxygen) facilitates an increase in the bubble size and leads to a quicker formation of bubbles in the glass melt (Table 2 and Fig. 1*b* ).

The processes occurring in the melting of diopside-hedenbergite mixtures can be analyzed using their reflection spectra. It is known [4, 6] that the $Fe^{3+}$ ions in the ultraviolet spectrum range show higher absorption than the $Fe^{2+}$ ions, and in the infrared range, $Fe^{3+}$ ions have lower absorption than $Fe^{2+}$ (the absorption is maximum at the wavelength 1100 nm). The ions $Cr^{3+}$ have the maximum transmission at the wavelength 550 nm, and the characteristic absorption bands are identified in the visible spectrum at the wavelengths 450 and 650 nm. The $Cr^{3+}$ ions exhibit high transmission in the red and infrared spectrum range, and the presence of $Cr^{6+}$ ions in this range of the spectrum does not have any effect on the transmitting capacity. Since with a light ray passing through a sample, the reflection angle is equal to the transmission angle, their spectra should be identical.

The study of the reflection spectra of the diopside-hedenbergite mixture in the visible range at different temperatures revealed the following (Fig. 2). The initial chromium-free iron-containing mixture has a high reflecting capacity. The initial mixture to which iron oxide is introduced as FeO has a gray color. With the temperature increasing to 1050°C, the reflecting capacity in the violet spectrum range decreases and in the near infrared range it increases. The mixture acquires a brownish-red color typical of the trivalent iron ions in the tetrahedral coordination. An increase in the temperature up to 1100°C decreases the reflecting capacity of the

sintered cake, but the nature of the spectrum remains the same. A further increase in temperature up to 1200°C abruptly decreases the reflecting capacity of the cake, i.e., increases its absorption, which is evidence of the increased content of bivalent iron. The cake acquires a black color typical of the $Fe^{2+} - O - Fe^{3+}$ chromophore group with a high concentration of the coloring agent. At a temperature of 1450°C, the absorption capacity increases even more. This suggests that within the interval of intense foaming of the mixture at a temperature of 1100 – 1200°C, the valence of the iron ions changes toward its reduction.

Introduction of chromium oxide to the mixture of the diopside-hedenbergite composition increases the reflecting capacity of the initial mixture, and this is the most perceptible in the infrared range (Fig. 2b, c). In this case, the spectra exhibit the maximum at a wavelength of 540 nm, which is typical of the trivalent chromium ion. That is why the initial mixture is colored green. With increase in temperature up to 1050 – 1100°C, this reflection maximum is shifted to the region of shorter waves. The sintered cake retains its green color, but at the same time, a brownish tint emerges in it. At a temperature of 1200°C the color becomes dark brown, and at 1450°C it becomes black. Simultaneously, the maxima typical of trivalent chromium in the reflection spectra disappear, and the absorption is significantly increased, which testifies to a more active coloring role of the $Fe^{2+} - O - Fe^{3+}$ chromophore,

In using iron-containing wollastonite glass compositions based on Krasnoyarsk power plant ashes, no increase in the thickness of the frothed glass melt layer was observed as the temperature increased (Fig. 1c). This can be explained by the fact that iron in such ashes usually exists (according to x-ray phase analysis) not as oxides but as ferrous meta- and orthosilicates and aluminoferrites. The authors who studied the processes of silicate and glass formation in the glass batches based on power plant ashes, nonferrous metallurgical slags, and mineral rocks registered the preservation of the silicate groups up to the melting point, and also identified the formation of additional pyroxene groups which melt at high temperatures. The iron in these groups usually exists in the bivalent state. Therefore, no intense frothing occurs in the series of wollastonite compositions synthesized from the Krasnoyarsk power plant ashes. Moreover, the high silicon oxide and aluminum content and the presence of fluorine increase the melt acidity, which facilitates the conservation of the bivalent iron in the melt.

A fluorine additive to the iron-containing wollastonite glass results in quicker melting of the mixture, clarification of the glass melt at lower temperatures (Fig. 1c), and a decrease by 50°C in the temperature interval of intense melt frothing (Table 2). As the fluorine content increases, the bubble size grows, but it does not cause a change in the thickness of the frothed glass melt layer since the large bubbles quickly leave the melt.
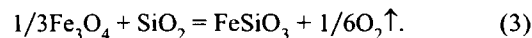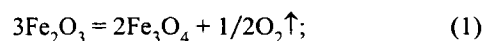
Thus, if we assess the foaming capacity of the iron-containing glasses based on the temperature interval of intense

foaming, we can see in Table 2 that augite-hedenbergite ($\Delta t = 50°C$) and iron-containing wollastonite mixtures with a fluorine additive ($\Delta t = 100°C$) have the narrowest interval of foaming temperatures. These mixtures are the most promising for industrial glass-melting. The average intense foaming interval of the glass melts of the hedenbergite and diopside-hedenbergite (with 1,5% $Cr_2O_3$) mixtures is equal to 150°C. The least suitable are chromium-free diopside-hedenbergite mixtures and mixtures with a low content of chromium oxide, since they have a substantial temperature interval of foaming, which calls for lengthening of the melting zone in glass-melting furnaces.

If we assess the iron-containing glasses based on the frothed layer thickness, we can see in Table 2 that the hedenbergite and diopside-hedenbergite mixtures show an increased tendency to foam formation. The augite-hedenbergite and the iron-containing wollastonite mixtures do not exhibit an increase in the thickness of the frothed glass layer, and yet bubbles are formed during the batch melting and the melt clarification.

Thus, in assessing the foaming intensity on the basis of the two parameters, i.e., the foaming temperature interval and the frothed layer thickness, the augite-hedenbergite and the iron-containing wollastonite glass compositions are found to be the most promising for practical use.

The analysis performed and the regularities discovered suggest that foaming in the iron-containing glasses is caused by excessive emission of oxygen in melting, i.e., when the liquid phase emerges at the temperatures of 1150 – 1250°C. Within this temperature interval, according to the x-ray phase analysis data, the quartz grains intensely dissolve in the liquid phase saturated with iron ions. According to the thermodynamic calculations, the following reactions involving the emission of oxygen are possible (Fig. 3):

$$3Fe_2O_3 = 2Fe_3O_4 + 1/2O_2\uparrow; \qquad (1)$$

$$2/3Fe_3O_4 + SiO_2 = Fe_2SiO_4 + 1/3O_2\uparrow; \qquad (2)$$

$$1/3Fe_3O_4 + SiO_2 = FeSiO_3 + 1/6O_2\uparrow. \qquad (3)$$

It was demonstrated in [7] in studying the formation of bubbles as a result of the chemical reactions in the clarifying glass melt that bubble formation becomes possible when the pressure of the released gases exceeds 1 MPa. If the gas pressure stays within the interval of 0.1 – 1 MPa, the emitted gases will join the bubbles already existing in the melt and contribute to their growth, since the pressure inside the bubbles will always exceed 0.1 MPa:

$$p_g = p_{atm} + \gamma h + 2\sigma/r,$$

where $p_g$ is the gas pressure inside the bubbles; $p_{atm}$ is the atmospheric pressure; $\gamma h$ is the liquid column pressure above the bubble; $\sigma$ is the surface tension; $r$ is the bubble radius.
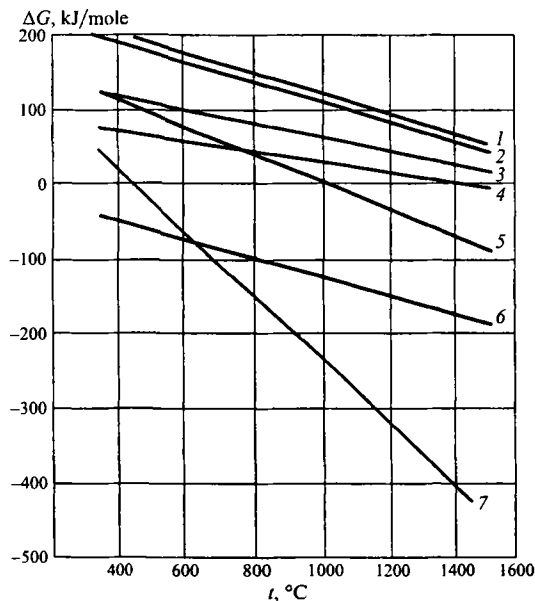
**Fig. 3.** Dependence of isobaric-isothermic potential $\Delta G$ on temperature $t$ for reactions: $1$) $Fe_3O_4 = 3FeO + 1/2O_2$; $2$) $Fe_2O_3 = 2FeO + 1/2O_2$; $3$) $Fe_2O_3 + + SiO_2 = Fe_2SiO_4 + 1/2O_2$; $4$) $2/3Fe_2O_3 + SiO_2 = Fe_2SiO_4 + 1/3O_2$; $5$) $3Fe_2O_3 = 2Fe_3O_4 + 1/2O_2$; $6$) $2/3Fe_3O_4 + SiO_2 = Fe_2SiO_4 + 1/3O_2$; $7$) $1/3Fe_3O_4 + SiO_2 = FeSiO_3 + 1/6O_2$.
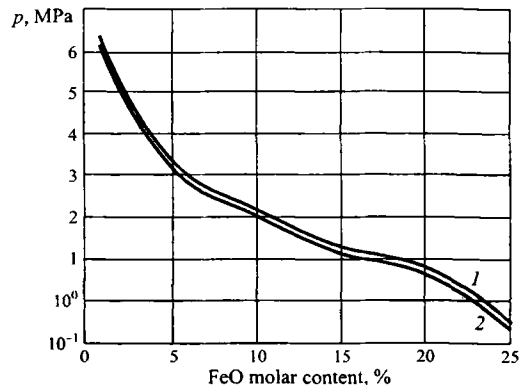


**Fig. 4.** Dependence of released oxygen pressure in the glass melt in the course of melting on the FeO content in the iron-containing glass mixture at temperatures of 1100 ($1$) and 1200°C (2).

With a lower pressure level (0.01 – 0.1 MPa), the bubbles should not emerge at all, since in these conditions the melt approaches the equilibrium state with respect to all gases contained in the glass melt.

According to the x-ray phase analysis, FeO introduced to the mixture becomes fully oxidized to $Fe_2O_3$ at a temperature of 800°C. Thus, it can be assumed that as the temperature increases, reaction (1) should be the first, and reactions (2) and (3) should follow, but as reaction (3) is thermodynamically the most probable, the pressure of the oxygen emitted in the course of the reactions in the present study was calculated on the basis of reaction (3). It was assumed in the calculation that 0.25 mole fractions of $SiO_2$ enter into the reaction (the excess $SiO_2$ remaining in the main components of the batch after the completion of the silicate-formation processes) [7]. The equilibrium constant $K_c$ at temperatures of 1100 and 1200°C was calculated based on the change in the isobaric-isothermic potential $\Delta G$ of reaction (3) using the equation in [8]:

$$\log K_c = - \Delta G/(4.576T).$$

The mass action law for reaction (3) is

$$K_c = \frac{[FeSiO_3]p_{O_2}^{1/6}}{[Fe_3O_4]^{1/3}[SiO_2]}.$$

Reaction (3) was used to calculate the pressure of oxygen for the concentration of FeO introduced into the iron-con-

taining glass mixtures. It is seen in Fig. 4 that with an FeO content in the mixture up to 15 mole %, the oxygen pressure will be above 10 MPa. This pressure is sufficient for the formation of bubbles in the glass melt. A further increase in the iron oxide concentration results in a decrease in the partial oxygen pressure in the melt, as a consequence of which the iron oxide converts to a more reduced form. It follows from here that in order to prevent foaming during the melting of iron-containing glasses, the iron should be present in the melt in the form of FeO. For this purpose, the following conditions have to be satisfied:

the glass matrix should be sufficiently acid (basicity-acidity modulus not more than 0.8);

melting of iron-containing glasses should be carried out under reducing conditions;

for the purpose of glass melting, it is expedient to use ashes and slag from thermal power plants, nonferrous metallurgical slag, and other wastes containing silicate and aluminate compounds in which iron exists mostly in the bivalent state.

For the purpose of preventing the foam from escaping from the melting zone to the working zone, in designing gas-flame furnaces for melting iron-containing glasses, it is necessary to provide for special barriers or foam-capturing pockets in front of the working area. In order to attain the reducing conditions before glass working, it is necessary to ensure a positive pressure of smoke gases in the gas chamber of the working zone of the furnace.

Since according to the reaction of oxygen emission presented above, the process of bubble formation during the iron oxide reduction takes place not only in the surface layers of the melt but in the deeper layers as well, the process of bubble release in the stage of melting of iron-containing mixtures has to be intensified. The direct-flow furnaces providing for the glass melt clarification in a thin layer [9] are the most suitable for this purpose. This will not only reduce the time of bubble rise to the melt surface, but will also decrease the temperature gradient across the depth of the iron-containing glass melt.

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